CHAPTER 6

DISSOLVED, PARTICULATE AND BED SEDIMENT GEOCHEMISTRY OF TRACE ELEMENTS AND REEs IN THE SWARNA ESTUARY, SOUTHWEST COAST OF INDIA
ABSTRACT

The studies on tropical estuarine geochemistry are limited to heavy metal analysis. This study focuses on the abundance of trace elements and rare earth elements (REEs) along the salinity gradient in a tropical estuary on a seasonal scale. The Swarna estuary is studied to understand the behaviour of trace elements and REEs in the dissolved, particulate and bed sediment phases and their distribution fractions between the three phases along the salinity gradient. The dissolved trace elements like B, Rb, Sr, Se, Cr, Mo, As, Cs, Pb and U increase with salinity. The dissolved trace elements like Sr, B and Rb show conservative nature. Although the dissolved fractions of Cr, Mo, As, V, Cs, Pb, U and Nb show an increase along the salinity gradient, they show non-conservative behavior due to their sorption on to the SPM under the alkaline condition. The dissolved Fe undergoes flocculation in the Swarna estuary. The dissolved Mn is found to be controlled by dissolved organic carbon forming colloidal organic carbon – metal complex which in turn acts as a scavenger to other metals present in the estuarine water. This is also supported by the dominance of Mn in the SPM phase compared to the dissolved and bed sediment phases. Dissolved REEs show identical behaviour with changing salinity for the three sampling seasons with their availability being controlled by the prevailing pH conditions. It is found that the estuarine suspended particulate matter (SPM) at the sea water front (30.4 ‰) of the Swarna estuary has higher radiogenic strontium isotopic ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) and lower strontium concentration compared to the estuarine water which suggest the conservative transport of particulate material from the continent towards the sea. The $^{87}\text{Sr}/^{86}\text{Sr}$ in the bed sediment represents the dominant silicate signature of the basin. The study determines the dominance of coastal groundwater discharge over the dissolved trace elements and REEs during the low river discharge season in the Swarna estuary.

Keywords: Trace element, Rare earth element, Strontium isotope, Tropical estuary, Swarna estuary, Southwest coast of India.
6.1. INTRODUCTION

Estuaries play a crucial role in the geochemical cycling of elements at the earth’s surface. The dynamicity of estuaries are not limited to river runoff or tidal mixing, but also involves various internal physical, chemical and biological processes which govern the chemical composition of water and sediments as well as the fate of terrestrial elements being transported to the sea. The estuarine geochemical studies help in determining whether the riverine flux of element goes unchanged into the ocean or gets added/removed during its passage through the estuary (Honeyman and Santschi, 1988; Santschi et al. 1997). The biogeochemical processes occurring in the estuaries promote the inorganic or organic removal or addition of elements from or to the solution which affect their conservative or non conservative nature. Recent geochemical and isotopic studies on the estuarine waters suggest submarine groundwater discharge as an additional source of elements to the coastal waters and nearby ocean (Charette and Sholkovitz, 2006; Beck et al. 2007; Jeong et al. 2012; Kim and Kim, 2014). Thus, the study on estuarine geochemistry needs a careful assessment of source contribution and in-depth study of each driving factor in the complex aquatic system. This study is intended to discuss the geochemical behaviour and the fate of trace elements in a relatively pristine estuarine system of west coast of India.

West coast of India is one of the rapidly developing regions of India with densely populated cities and major industries located all along the coast. The Swarna River is studied for its estuarine geochemical characteristics and behaviour on a seasonal basis. The main objectives of this work are (1) to determine the role of physico-chemical parameters and dissolved organic carbon on the behaviour and fate of trace elements and rare earth elements along the salinity gradient, (2) to assess the distribution of metals between the dissolved, suspended particulate matter and bed sediment phases of the estuary and (3) to determine the sources of elements being transported by the estuarine water.

6.2. RESULTS AND DISCUSSION

6.2.1. Physico-chemical characteristics

The results on the physico-chemical characteristics of the Swarna estuary are given in Table 6.1 and Fig. 6.1. The water samples collected from the Swarna estuary during
January 2011 (post-monsoonal season), May 2011 (pre-monsoonal season) and October 2011 (monsoonal season) show a significant difference in physico-chemical parameters which could be attributed to the mixing trend of fresh water and sea water throughout the estuary. The Swarna estuary could be categorized under the well-mixed estuary as there is a uniform mixing of fresh water and the sea water which could be observed from the salinity gradient (0.03 – 34.7 ‰) measured for the estuarine water during the sampling seasons and due to the shallow depth. However, the mixing of river water with sea water is found to be negligible during the pre-monsoon season due to low river discharge. Moreover, the downward river flow is found to be completely obstructed by the Baje dam at Hiriyadka, Udupi during the dry sampling season. This led to the inflow of saline water up to 25 km inland till Baje, Hiriyadka. As a result, the minimum salinity in the estuary at the freshwater front is measured to be 17.7 ‰ for the pre-monsoon season. The dilution in salinity of sea water in the freshwater front would have occurred due to the inflow of groundwater to the estuarine region during the pre-monsoon season. The temperature of estuarine water varies from 27.3 to 29.8 °C, 30.4 to 33.9 °C and 28.3 to 31.5 °C during the post-monsoonal, pre-monsoonal and monsoonal sampling seasons respectively. Water temperature shows an increase by 0.5 – 1 °C between 0 and 2.5 ‰ of salinity and thereafter gradually decreases with a slight variation due to continuous mixing of sea water during the monsoonal and post-monsoonal sampling. There is a relatively higher variability in temperature along the salinity gradient during the pre-monsoon season compared to other two seasons. Although the variability of water temperature is less along the salinity gradient during each sampling season, there is a significant difference in temperature with season, with almost a parallel linear decreasing trend along the increasing salinity gradient. The pH of estuarine water ranges from 7.2 to 8.1, 7.5 to 8.2 and from 7.4 to 8.1 during the post-monsoonal, pre-monsoonal and monsoonal sampling seasons respectively. The similar increasing trends in pH along the salinity gradient are observed for post-monsoon and monsoon seasons. Although the pH of pre-monsoon season increases along the salinity gradient (24 to 34.7 ‰), it exhibits relatively lower values particularly between the region of 19 and 33 ‰ salinity during the pre-monsoon season. The contrasting less alkaline nature (relatively lower pH) during the pre-monsoon season compared to other seasons suggests higher groundwater contribution to the estuarine water (Pempkowiak et al. 2010). The pH of estuarine water increases sharply at the sea water front during the pre-monsoon season to represent the alkaline nature of sea water. The slightly alkaline pH (7.8) at 17.7 ‰ salinity could be due to the photosynthetic activity of
the in-situ phytoplankton at the less turbulent zone (freshwater front) of the estuary during the pre-monsoon season. The less momentum of water would have supported the higher phytoplankton growth, and the well lit condition (as observed from higher temperature) would have resulted in the higher photosynthetic activity at the region of 17.7 ‰ salinity. This is also justified with the observed higher dissolved oxygen (DO) and dissolved organic carbon (DOC) concentration for the same season (Fig. 6.1). The DO in estuarine water varies from 6.3 to 6.9 mg L\(^{-1}\), 6.7 to 7.03 mg L\(^{-1}\) and from 6.3 to 7.83 mg L\(^{-1}\) during the post-monsoonal, pre-monsoonal and monsoonal sampling seasons respectively. The trend in DO variability is found to be similar during the post-monsoonal and monsoonal seasons with lower DO at mid salinities and higher DO at both fresh and saline water end members. DO of pre-monsoon sampling season follow the pH pattern. The DOC in estuarine water ranges from 1.77 to 2.42 mg L\(^{-1}\), 1.46 to 5 mg L\(^{-1}\) and from 0.68 to 4.67 mg L\(^{-1}\) during the post-monsoonal, pre-monsoonal and monsoonal sampling seasons respectively. DOC concentration measured along the salinity gradient during the post-monsoon sampling shows a slight increase in the mid salinity. A steep decrease in DOC concentration along the salinity gradient between 0 and 3.6 ‰ salinity is observed during the monsoonal season which could be due to the higher removal rate of DOC from the water column during the initial mixing whereas the DOC concentration increases at mid salinities between 13.5 and 27 ‰ of estuarine water. The decrease in DOC concentration along the salinity gradient during all seasons suggests the removal of terrestrial DOC brought by the rivers in the estuarine region. The increase in DOC concentration at the mid salinities would be due to the resuspension of DOC from the previously adsorbed metal oxy-hydroxides or SPM. The well-lit, less turbulent zone occurring at 17.7 ‰ salinity during the pre-monsoon season supports higher photosynthetic activity of phytoplankton which results in the sharp increase of pH, DO and DOC values. The absence in photosynthetic activity would have resulted in lower DO under the higher temperature condition of pre-monsoonal season. Thus, DOC in the estuarine water is found to be more of autochthonous in nature rather than allochthonous origin during the pre-monsoonal season. The SPM concentration in estuarine water ranges from 5.6 to 11 mg L\(^{-1}\), 10.6 to 15.4 mg L\(^{-1}\) and from 9.8 to 19.8 mg L\(^{-1}\) during the post-monsoonal, pre-monsoonal and monsoonal sampling seasons respectively. SPM increases in estuarine water along the higher salinity gradient in all seasons. Also, there is a significant addition of SPM at varying salinities of each sampling season which could be attributed to the resuspension of particulates from the bottom sediments. The high river discharge during the monsoonal
Figure 6.1: Physico-chemical parameters, SPM and DOC measured along the salient gradient for the study period in the Swarna estuary.

6.2.2. Dissolved major ions, trace elements and rare earth elements in the Swarna estuary

The trace elements and rare earth elements measured in the dissolved phase of the Swarna estuary are given in Table 6.2. The dominating trace elements in the Swarna estuary are as
6.2.2.1. Co-existence and behaviour of dissolved chemical species

The inter-relationships between physico-chemical parameters, trace elements and rare earth elements present in the dissolved phase (n = 25 samples) of the Swarna estuary are represented in the form of a dendrogram (Fig. 6.2) obtained through Centroid clustering method of Hierarchical cluster analysis and Pearson correlation technique of SPSS v.19.

The chemical species in the dendrogram are grouped into 6 cluster memberships to explain their geochemical behaviour and fate under changing physico-chemical conditions. The first group of elements combines with salinity showing very high correlation ($r = 0.7 – 0.99$ at $p < 0.05$ i.e., 95 % confidence level). The salinity combines with trace elements like Cs, Cr and Cd initially which later combines with V, Pb, Nb and Sb. These elements in turn combine with the cluster of major and minor elements including Ca, Mg, Na, B, K, Sr, Se and Rb. At a higher stage they group with elements like Ti, Ag, Te and Er together to form cluster membership - 1. The elements belonging to cluster membership - 1 are largely controlled by the salinity of estuarine water (Fig. 6.3). These elements maintain the signatures of the freshwater in the mixing zone throughout the estuary with their concentration being dependent mainly on the salinity of water. This suggests that the sources of these elements could be natural processes and have no additional anthropogenic sources in the estuarine region. The concentrations of elements like B, Sr and Rb show a linear increase with salinity representing the conservative nature in the estuarine water whereas Se show slightly non-conservative nature. The concentrations of other elements clustering with salinity in the dendrogram also show an increase with salinity, but are highly affected by the pH variability at higher salinity front and higher SPM (particularly

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during the monsoonal season) which indicates the metal sorption behaviour mainly under the alkaline condition in the estuary.

Most of the rare earth elements like Pr, Nd, Tm, Eu, Ho Sm, Dy, Lu and Yb show a good correlation \((r = \pm 0.4 \text{ to } 0.9)\) with trace elements like As, U, Co, Mo, Ga and P which group to form cluster membership – 2 in the dendrogram. They combine with elements of cluster membership – 1 at a higher stage which indicates that the elements of cluster membership – 2 are also controlled by salinity of the estuarine water and have no additional anthropogenic sources contributing to their concentration variability in the estuary. These elements also show a good correlation with pH indicating the pH mediated sorption behaviour of REEs at different salinities (Fig. 6.4). It is found that the concentrations of REEs increase along the salinity gradient with the increase in pH up to 7.7 – 8.0 units, and thereafter a sharp decrease in REEs concentration is observed under the alkaline condition with the increase in salinity of the estuarine water. This could be due to the dominance of sea water signature over the REEs concentration at higher salinity. The seasonal variability of estuarine REEs concentration and its higher variability along the salinity during the same season are further examined by determining its possible sources in the estuarine region. The concentrations of dissolved REEs in coastal rain water (Santhekatte), downstream river water (Puthige; surface water source) and coastal groundwater are compared with that of the estuarine water to understand the higher variability of the REEs present in the estuary along the salinity gradient (Fig. 6.5). It is observed that the REE pattern in the estuary during the monsoonal season show similar trend with rain water. The estuarine REE patterns during the non-monsoonal seasons follow more of the REE patterns of the coastal groundwater. This suggests that the groundwater discharge could be the dominant source for these elements in the estuarine region particularly during the non-monsoonal seasons. This in turn would have resulted in higher concentration of REEs along the salinity gradient in the estuarine region.
Figure 6.2: Dendrogram explaining the behaviour of dissolved trace elements in the Swarna estuary.
Figure 6.3: Dissolved trace element variability along the salinity gradient during the three sampling period in the Swarna estuary.
Figure 6.4: Relationship of rare earth elements (ng kg$^{-1}$) with pH and salinity (‰).
Figure 6.5: Representation of source contributions to estuarine REEs for the sampling period.
The cluster membership – 3 shows association of DO with DOC and elements like Be and Gd (Fig. 6.2). Although Be and Gd are associated with DOC in the dendrogram, Be shows a good correlation with Fe \( (r = -0.4, p < 0.05) \) and other redox sensitive metals \( (r = 0.55 – 0.73, p < 0.05 \text{ with As and Mo}) \) whereas Gd shows a significant correlation \( (r = 0.42, p < 0.05) \) only with Mo. DOC in the estuary is largely dependent on the DO of water (Fig. 6.6). DOC concentration decreases with increasing DO during the post-monsoonal season. The decreasing trend of DOC with increasing DO is found to be highly affected by the photosynthetic activity of the phytoplankton during the pre-monsoon season. This results in the overall low positive correlation \( (r = 0.43, p < 0.05) \) between DO and DOC of the estuarine water for the sampling period as the photosynthetic activity leads to higher DOC along with higher DO and pH conditions.

![Figure 6.6: Relationship of DO with DOC in the Swarna estuary during the sampling period.](image)

DOC shows a good correlation with Fe, Mn, As and Mo \( (r = 0.46 – 0.7, p < 0.05) \) which are known to be sensitive to redox processes. The relationship of DOC with Mn could be observed by the combination of cluster membership \( – 3 \) with cluster membership \( – 4 \). As the Mn and Fe are released to the dissolved phase from the oxy-hydroxide state under the less oxidized condition, they tend to form metal complexes with DOC. The positive correlation of Fe \( (r = 0.69) \) and Mn \( (r = 0.46) \) with DOC suggests that the DOC involved in metal complexation are mainly organic colloids of smaller size (Buffle and Leppard, 1995) which allow the colloidal organic carbon – metal complexes to remain in the dissolved mode until they coagulate to form larger aggregates (Ran et al. 2000; Pourret et al. 2007)
and settle at the bottom of the estuary. However, Fe shows a significant correlation with temperature in the estuarine water with $r = 0.74$ at $p < 0.01$. This supports the close clustering relationship of DOC with Mn and only at higher stage with Fe in the dendrogram. Thus, the effect of DOC is relatively higher on Mn compared to Fe in the Swarna estuary. DOC in the estuarine water is found to be of similar characteristics as that of river DOC with formation of labile organic carbon - metal complexes, except the dominance of DOC over the Mn concentration in the estuary unlike the dominance of river DOC over the Fe concentration (Tripti et al. 2013). The difference in the behaviour of Fe in the estuarine water would have occurred due to the flocculation property of dissolved Fe in the mixing zone (Sholkovitz 1976; Boyle et al. 1977; Crerar et al. 1981).

As and Mo show a good negative correlation ($r = -0.46$ and $-0.48$, $p < 0.05$) with DOC suggesting the removal of these elements by the organic carbon - metal complexes (Fig. 6.7). However, these redox sensitive elements show a poor correlation ($r < 0.4$, $p < 0.05$) with DO in the Swarna estuary. DO, which is mainly controlled by temperature, could be altered by the higher photosynthetic activity of the phytoplankton. This in turn results in higher DO, higher pH and higher DOC under higher temperature condition. The control of DO by temperature as well as biological activities would have resulted in less correlation of DO with metal concentration in the estuarine water as these parameters in turn have higher effect on the metal availability in the estuarine water. As and Mo are showing a good association with salinity (cluster membership – 1) whereas Mn with pH (cluster membership – 4) and Fe with temperature (cluster membership – 6) in the dendrogram. The relationship of Mn and Fe with their controlling parameters is shown in Fig. 6.8. The association of Mn with pH and DOC suggests the effect of photo-reduction of Mn oxides by the DOC which could supply the dissolved Mn required for the photosynthetic activities of the phytoplankton (Sunda et al. 1983). The higher Mn concentration associated with higher pH, DO and DOC concentrations in the freshwater front (17.7 ‰ of salinity) of the estuarine water during the pre-monsoon season support the photo-reduction of Mn oxides in the Swarna estuary. Mn combines with La and at a higher stage clusters with Ce and SPM which later shows association with pH, Ta and Si, together to form the cluster membership - 4. Mn show good correlation with Ce ($r = 0.57$, $p < 0.01$) whereas Ce shows good correlation with Ta and La ($r = 0.8 - 0.9$, $p < 0.01$). Mn being redox sensitive, forms colloidal oxy-hydroxide which acts as a potential source for metal cation adsorption in the natural environment (Sholkovitz and Copland 1982; Sigg 1985; Balistrieri et al. 1994).
The clustering of Mn with Ce in the dendrogram and also a positive correlation between them indicates that Mn has a significant control over the Ce abundance under the redox conditions in the Swarna estuary (Fig. 6.9).

Figure 6.7: Relationship of DOC with As and Mo.

Figure 6.8: Representation of the controls of temperature (°C), pH and DOC (mg L\(^{-1}\)) on Fe (µg kg\(^{-1}\)) and Mn (µg kg\(^{-1}\)) concentrations.
Figure 6.9: Association of Mn with redox sensitive Ce in dissolved phase of the Swarna estuary.

SPM shows good correlation \( (r = 0.4 - 0.7 \text{ at } p < 0.05) \) with most metals (Fig. 6.10) belonging to the cluster membership – 1 which are controlled by salinity. SPM is highly correlated with pH \( (r = 0.63, p < 0.01) \) than salinity \( (r = 0.55, p < 0.01) \) which is represented by the cluster membership – 4 suggesting the possible effect of pH mediated geochemical processes on the SPM concentration in the estuarine water. In addition, the colloidal organic carbon - metal complexes would be contributing to the SPM at a higher rate under the alkaline condition. Si shows good correlation with pH \( (r = -0.57 \text{ at } p < 0.01) \) than salinity \( (r = -0.37 \text{ at } p < 0.05) \) suggesting that the Si is being removed under alkaline condition which could be controlled even by the biological processes occurring in the estuarine water. The variability of pH from near neutral to alkaline condition \( (7.2 < \text{pH} < 8.2) \) in the estuarine water could significantly affect the metal abundance (Shiller and Boyle 1985; Gaillardet et al. 2003) as it controls the metal sorption processes in natural waters. pH shows a good correlation \( (r = 0.4 - 0.9 \text{ at } p < 0.05) \) with elements belonging to cluster membership – 1 which suggests that these metals are highly affected by pH driven sorption reactions at different salinities in the estuarine water (Fig. 6.10). This is also supported by the concentration variability of each metal in different seasons. Although the concentrations of trace elements belonging to cluster membership – 1 show an increase with salinity in all the seasons, there is a significant variability in the concentration of each metal at different salinities during the monsoonal season. This could be attributed to the pH mediated sorption processes which affect the concentration of these metals at different
salinities. The effect of sorption processes is found to be varying with season and is relatively higher during the monsoonal season followed by pre-monsoon season and lesser during the post-monsoon season. The higher effect of sorption processes on the trace elements concentration in the estuary during the monsoonal season could be due to the higher pH variability at the mixing zone. The pH of Swarna river water is found to be slightly acidic to near neutral (Tripti et al. 2013). The mixing of higher amount of near neutral freshwater with the alkaline sea water within the short distance would have resulted in the significant effect on the trace element behaviour in the estuary during the monsoonal season. The trace elements like Cr, Pb, Ti, Nb, V, U, Cd, Sb, Ag, Cs and Se are found to be highly affected by such processes in the Swarna estuary.

The cluster membership – 5 shows association of trace metals like Zr, Al, Hf, Tl and Ni. Al shows no significant correlation with Zr, Hf, Tl and Ni at p < 0.05 whereas it shows a good positive correlation (r = 0.4 – 0.6, p < 0.05) with temperature, Fe and Mn which suggests that Al could behave similar to Fe and Mn under redox conditions. Al oxy-hydroxide acts as the potential particle surface for the adsorption of metals like Zr, Hf, Tl and Ni in the estuarine water. However, Al show poor correlation (r = 0.35 at p < 0.05) with DOC unlike Fe and Mn. The cluster membership – 5 represents the group of lithophile elements which are more resistant to weathering and highly immobile in nature. The elements of cluster membership – 5 further combine with elements of cluster membership – 6 at a higher level. The cluster membership – 6 in the dendrogram represents the association of temperature with Fe, Cu, Ba and Zn. The relationship of Fe with temperature is also shown in Fig. 6.8. This suggests that the temperature driven redox processes control the behaviour of these elements in the estuarine water. Fe and Ba which are sensitive to redox conditions, acts as the metal scavenger to other trace metals like Cu and Zn respectively in the Swarna estuary (Fig. 6.11). The association of metals like Fe, Cu and Ba is also observed in the Swarna river water (Tripti et al. 2013). Thus, the understanding of biogeochemical processes controlling the behaviour of trace elements in the estuarine water needs a careful assessment of each driving parameter whereas the linear relationship of metals with single controlling parameters would not be sufficient to explain the biogeochemistry of estuarine water.
Figure 6.10: Relationship of pH, SPM (mg L\(^{-1}\)) and trace elements (µg kg\(^{-1}\)) in the dissolved phase of the Swarna estuary.
6.2.2.2. Dissolved strontium and its isotope ratio

The Sr concentration and its isotopic ratio measured in the dissolved phase of Swarna estuary are given in Table 6.3 and Fig. 6.12. It is observed that the dissolved Sr behaves conservatively along the salinity gradient in the Swarna estuary (Fig. 6.12.a). The dissolved Sr concentration increases linearly with salinity during the three sampling periods. The concentrations of Sr are almost similar for the same salinity during the three sampling seasons. A slight decrease in concentration at the freshwater front of the estuary is observed during the monsoonal sampling. The decrease in dissolved Sr concentration could be due to the dilution effect resulting from the higher river water discharge during the monsoonal season. It is found that the radiogenic Sr isotope ratio gradually decreases as the water moves from fresh water end member to sea water end member (Fig. 6.12.b). For the monsoonal season, the decreasing rate is higher at the initial mixing of fresh water with the saline water between 0.5 and 3 % of salinity; thereafter the isotopic ratio decreases slightly with a gentle linear slope ($r^2 = 0.84$) towards the sea water end member.
Figure 6.12: Strontium concentration (a) and its isotopic ratio (b) in the dissolved phase along the salinity gradient for the sampling period.

Figure 6.13: Isotope systematics of dissolved strontium in the Swarna estuary during the study period.

6.2.3. Sediment geochemistry of the Swarna estuary

The major elements, trace elements and rare earth elements measured in suspended particulate matter (SPM) and bed sediments of the Swarna estuary are given in Table 6.4. The concentrations measured for these elements in the estuarine bed sediment and SPM supports the explanation on dissolved trace elements in the Swarna estuary for the study period.
the bed sediments, unlike the dissolved phase of the Swarna estuary for the study period. Strontium in the bed sediment samples behaves distinctly in different seasons. The Sr concentration decreases with increasing salinity during the pre-monsoonal season whereas it tends to increase along the salinity gradient during the monsoonal season. This increase in Sr concentration could be due to the addition of Sr which first occurs at a lesser rate between 0.4 and 13.5 ‰ of salinity and then a significant addition between 17 and 30 ‰ of salinity during the monsoonal sampling (Fig. 6.14). The addition of Sr to the bed sediments has not affected the conservative Sr in the dissolved phase. This suggests that the additional Sr to the bed sediments would have been contributed by the SPM or the less weathered sediments are being transported to greater distance during the monsoonal season. The latter effect could be less as the bed sediments exhibit lesser radiogenic Sr isotope ratio with increasing salinity and thus, indicates the SPM contribution. This could be the reason for the variability of SPM concentration measured at these salinities during the monsoonal season. The SPM of monsoonal season measured for the sea water front (at 30 ‰ of salinity) exhibit relatively lower Sr concentration (Fig. 6.14.a) and relatively higher radiogenic Sr isotope ratio (Fig. 6.14.b and Fig. 6.15) compared to the sea water ($^{87}$Sr/$^{86}$Sr = 0.7091) suggesting that the estuarine SPM in the sea water front is still of terrestrial origin, and that the terrigenous SPM is being transported to the ocean. A gradual decrease in Sr concentration of the bed sediment with increasing salinity is observed between 17 – 34 ‰ during the non-monsoonal season which follow the similar pattern of monsoonal sampling between 13 – 17 ‰ of salinity. This could be due to the removal of Sr from the estuarine bottom sediments during the high tides of pre-monsoon season when there is less fresh water input to the sea; thus leading to higher SPM concentration at the saline water end member. Hence, the Sr concentration and its isotopic ratio in SPM of the Swarna estuary suggests that the increase in the SPM concentration along the higher salinity gradient in different seasons could be due to the resuspension of particulates from the bottom sediments, and the marine particulate input is negligible. The $^{87}$Sr/$^{86}$Sr measured in bed sediments and SPM of the Swarna estuary explains that the terrestrial materials brought by the river are being transported through the estuarine region towards the ocean and the marine influx is less.
Figure 6.15: Isotope systematics of strontium in bed sediments (BS) and SPM of the Swarna estuary during the study period.

6.2.3.2. Elemental distribution between dissolved and particulate phases

The partitioning of trace elements between the dissolved and particulate phases results in the redistribution of trace elements in the aquatic system. The factors controlling the partitioning of trace elements between surface water and sediments in the Swarna estuary mainly include pH, redox condition, organic content, temperature and biological activities. The distribution coefficient for the chemical species is calculated as follows (Valenta et al. 1986): $K_d = \frac{C_{SPM}}{C_{DP}}$, where $C_{SPM}$ is the concentration ($\mu g \ kg^{-1}$) of trace elements in the suspended particulate matter and $C_{DP}$ is the concentration ($\mu g \ kg^{-1}$) of trace elements in the dissolved phase. As the trace elements are measured only in one SPM sample of 30‰ salinity (sea water front) collected during the monsoonal season, the $K_d$ is measured for this sample. The sample of sea water front in the estuary shows different $K_d$ values for different elements which could be classified into seven groups (Table 6.6). The $K_d$ values suggest that the SPM is dominated by colloidal Fe oxy-hydroxides followed by Al and Mn oxy-hydroxides or the colloidal metal-organic carbon complexes in the sea water end member of the Swarna estuary. The ratio of chemical species between bed sediment and SPM in the sea water end member shows that the trace elements like Zn, Te and Mn are relatively enriched in SPM than bed sediments whereas Sn, Cu, Tl, As, Pb, Cs, B and Mo in SPM have almost the bed sediment composition. The depletion in SPM relative to bed
sediments are found to be 50 % for elements like P, Ni, Sb, Fe, Mg, Ga, Al, Cd, Rb, Co, W, Tm, V, Er, Dy, Ho, Yb, Eu, Gd and Be and 70 % for Lu, Ti, Sm, Nd, Pr, Cr, Na, La, Zr, Th, K and U. The bed sediments are found to be three times enriched with Nb, Sr, Ce, Hf, Ba, Ag, Ta and Ca relative to its suspended particulate phase. The dominance of colloidal metal oxy-hydroxides and metal-organic carbon complexes support the relatively higher SPM concentration measured at the sea water front than the fresh water front during its transport in the Swarna estuary for the study period.

Table 6.6: Distribution coefficient ($K_d$) for trace elements and REEs at the sea water front in the Swarna estuary.

<table>
<thead>
<tr>
<th>Group</th>
<th>Ratio</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.1 &lt; K_d &lt; 10$</td>
<td>Se, Mg, B</td>
</tr>
<tr>
<td>2</td>
<td>$10 &lt; K_d &lt; 10^2$</td>
<td>Sr, K, Ca, Mo</td>
</tr>
<tr>
<td>3</td>
<td>$10^2 &lt; K_d &lt; 10^3$</td>
<td>Rb, Cs, Tl, Te, W, U, Sb</td>
</tr>
<tr>
<td>4</td>
<td>$10^3 &lt; K_d &lt; 10^4$</td>
<td>Pb, Tm, Cs, P, Ta, Lu, Nb, Ag, Be, Ho, Eu, As, Yb, Er, Cr, Ba, Hf</td>
</tr>
<tr>
<td>5</td>
<td>$10^4 &lt; K_d &lt; 10^5$</td>
<td>Gd, Ga, Pr, Sm, Zn, Dy, Co, Nd, Cu, V, Ni, La</td>
</tr>
<tr>
<td>6</td>
<td>$10^5 &lt; K_d &lt; 10^6$</td>
<td>Ce, Zr, Mn, Ti</td>
</tr>
<tr>
<td>7</td>
<td>$10^6 &lt; K_d &gt; 10^7$</td>
<td>Al, Fe</td>
</tr>
</tbody>
</table>

6.3. CONCLUSIONS

The study shows that most of the elements in the estuarine water maintain similar association with other metals as that of river water in the Swarna basin. This include: i) Pb and V which are discharge driven elements in the river water are controlled by the mixing of freshwater with sea water (salinity) in the estuary, ii) dominance of smaller size colloidal fractions of DOC both in river and estuary, iii) formation of colloidal organic carbon - metal complexes, particularly with Mn and iv) control of oxy-hydroxides of Fe and Ba over the heavy metals like Cu and Zn under redox conditions in the river and estuarine waters. The difference in the inter-metal association in the estuarine water and river water would have occurred mainly due to the pH variability. The near neutral to alkaline conditions and the relatively higher variability of pH with space in the estuary compared to that of the river water would have resulted in the adsorption/desorption of
trace elements in the estuarine system. The coastal groundwater discharge forms the main source of trace elements and REEs in the estuarine water, which is at a higher rate particularly during the pre-monsoon season.

REFERENCES


